

Synthesis, Crystal Structure, Theoretical Calculation, and Photophysical Property of a New Cd(II) Complex Based on N-heterocyclic Ligand and Isophthalic Acid^①

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ABSTRACT A new metal-organic coordination complex [Cd(imp)(*m*-bdc)]_n (**1**, ipm = 5-(1H-imidazo[4,5-*f*][1,10]phenanthrolin-2-yl)-2-methoxyphenol, *m*-bdc = isophthalic acid) has been synthesized by hydrothermal reaction and characterized by elemental analysis, thermogravimetric (TG) analysis, infrared spectrum (IR) and single-crystal X-ray diffraction. Complex **1** crystallizes in monoclinic, space group *C2/c* with *a* = 15.373(5), *b* = 16.719(5), *c* = 19.406(6) Å, β = 106.995(5)°, *V* = 4770(2) Å³, C₂₈H₁₈CdN₄O₆, *M_r* = 618.86, *D_c* = 1.724 g/cm³, $\mu(\text{MoK}\alpha)$ = 0.971 mm^{−1}, *F*(000) = 2480, *Z* = 8, the final *R* = 0.0391 and *wR* = 0.1044 for 4701 observed reflections (*I* > 2σ(*I*)). Single-crystal X-ray diffraction reveals that **1** exhibits a one-dimensional (1D) double-chain architecture, and the H-bond intersections link the 1D double-chain architecture into a 2D layer structure. TG analysis shows clear courses of weight loss, which corresponds to the decomposition of different ligands. We also study the luminescent properties of complex **1**. In addition, to elucidate the essential electronic characters of this complex, theoretical calculation analysis was performed by the PBE0/LANL2DZ method in Gaussian 03 Program.

Keywords: Cd(II) complex, crystal structure, fluorescence, theoretical calculation;

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1 INTRODUCTION

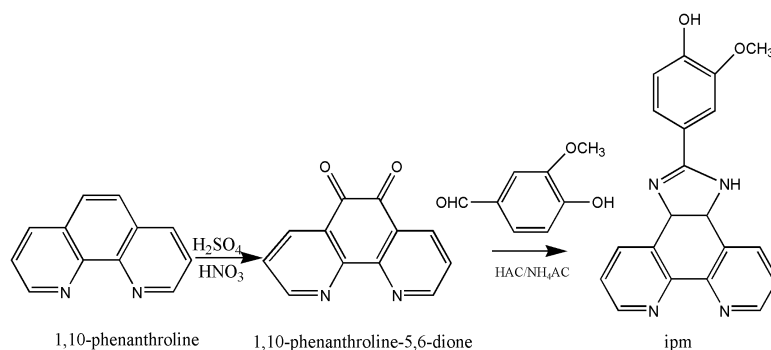
The crystal engineering of metal coordination polymers (MCPs) study is a very active and expanding research area for their rich structures and potential use as materials in catalysis, porosity, sensors, magnetism, luminescence, molecular recognition and so on^[1-5]. In this aspect, considerable progress has been made for controlling the topology and geometries of the networks to produce useful functional materials. It is well known that the assembly processes and structures of MCPs are determined by many factors, such as the coordination mode of metal ions, pH value of the solution, solvent systems, and so on. In this paper, we adopt hydrothermal method to

make ligands and metals self-assemble into coordination polymers through non-covalent bond interaction. Most of the complexes are synthesized by chelating nitrogen-containing ligands, such as 2-(pyridin-2-yl)pyridine, 4-(pyridin-4-yl)pyridine, 1,10-phenanthroline, 1,10-phenanthroline-5,6-dione, etc.^[6-9], and inorganic anions or organic carboxylic acids. Among poly-carboxylate ligands, the best studied are dicarboxylates, tricarboxylates, and biphenyldicarboxylate. In this paper, we design and synthesize a nitrogen-containing ligand using phenanthroline as a substrate: 5-(1H-imidazo[4,5-*f*][1,10]phenanthrolin-2-yl)-2-methoxyphenol (ipm), and the synthesis of ipm ligand is shown in Scheme 1:

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Scheme 1. Synthesis of ipm

From the coordination chemistry point of view, the dicarboxylic acid derivative is a versatile ligand since it offers strongly basic donor centers in ligand geometry facilitating chelating towards metal ions. It also constructs excellent supramolecular architecture with gorgeous artistic and valuable properties^[10-12].

As for Cd(II) ion, the chemistry of d^{10} metal clusters is of current interest for their flexible coordination environment, which can form complexes with variable geometries from tetrahedral, trigonal bipyramid, square pyramidal to octahedral. In this paper, we report a metal complex **1** with the derivative of 1,10-phenanthroline, namely, $[\text{Cd}(\text{ipm})(m\text{-bdc})]_n$.

2 EXPERIMENTAL

2.1 Materials and physical measurements

All chemicals were of AR grade and used without further purification. The contents of C, H and N were determined using a Perkin-Elmer 240C analyzer. TG measurements were performed on a NETZSCH STA 449C analyzer. IR spectrum was recorded in the range of $4000 \sim 400 \text{ cm}^{-1}$ on a Nicolet FT-IR 170SX spectrometer. The emission spectra were recorded on a FLSP 920 Edinburgh fluorescence spectrometer. ^1H NMR spectra of ligand were carried out with Bruker AV 300 MHz spectrometers and chemical shifts are referenced to internal TMS.

2.2 Synthesis of ipm ligand

The mixture of ammonium acetate (3.88 g, 50 mmol), 3-methoxybenzaldehyde, 1,10-phenanthroline-5,6-dione (0.525 g, 2.5 mmol), and glacial acetic acid was refluxed in distillation flask for 4 h and cooled to room temperature. Then when concentrated ammonia water is added to neutralize the solution to $\text{pH} = 7$, yellow precipitation can be obtained, and the precipitation can be washed with water and collected by filtration. The crude product dissolved in ethanol was purified

by silica gel filtration. Then, the solution was evaporated to get the yellow product ipm. The yield was 0.72 g (77%). m.p.: $318 \sim 325^\circ\text{C}$. ^1H NMR (CDCl_3 , ppm): 3.33 (s, 3H, $\text{CH}_3\text{-O-Ar}$), 3.60 (s, 1H, NH), 6.94 (m, 4H, Ar-H), 7.85 \sim 8.94 (m, 6H, aromatic protons in the moiety of phenanthroline, Ar-H). MS (ESI): $m/z = 343.1 [\text{M}+1]^+$, 365.1 $[\text{M} + \text{Na}]^+$.

2.3 Synthesis of $[\text{Cd}(\text{ipm})(m\text{-bdc})]_n$ (**1**)

A mixture of CdCl_2 (0.066 g, 0.3 mmol), ipm (0.110 g, 0.3 mmol), $m\text{-bdc}$ (0.10 g, 0.3 mmol) and H_2O (18 mL) was stirred at room temperature and the pH value was adjusted to 7.5 with NaOH, and then the cloudy solution was put into a 30-mL Teflon-lined stainless-vessel under autogenous pressure at 443 K for 72 h. Afterwards, it was cooled to room temperature at a rate of 5°C/h . The yellow crystals of **1** were collected in 74% yield based on Cd. $\text{C}_{28}\text{H}_{18}\text{CdN}_4\text{O}_6$: calcd. C, 54.34; H, 2.93; N, 9.05%. Found: C, 54.29; H, 2.94; N, 8.99%. IR (KBr, cm^{-1}): 3523(s), 1569(vs), 1384(vs), 1111(s), 1073(s), 912(s), 780(s), 727(s), 642(s), 536(m).

2.4 X-ray crystallography

A yellow crystal of complex **1** with approximate dimensions of $0.34\text{mm} \times 0.11\text{mm} \times 0.15\text{mm}$ was selected and mounted on a glass fiber. The diffraction data were collected at room temperature with a Bruker SMART APEX II CCD diffractometer equipped with a graphite-monochromatized $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at 293(2) K in the range of $1.84 \leq \theta \leq 26.10^\circ$ ($-18 \leq h \leq 18$, $-19 \leq k \leq 20$, $-15 \leq l \leq 24$) and 12861 were independent ($R_{\text{int}} = 0.0499$), of which 4701 observed reflections with $I > 2\sigma(I)$ were used in the succeeding structure determination and refinements. Data reductions and absorption were performed using the SAINT and SADABS programs, respectively. The structure was solved by direct methods with SHELXS-97^[13] and refined with SHELXL-97^[14] by full-matrix least-squares techniques on F^2 . The structure was refined by using anisotropic thermal parameters for all the non-hydrogen atoms to converge at $R =$

0.0391, and $wR = 0.1044$ ($w = 1/[\sigma^2(F_o)^2 + (0.1000P)^2]$, where $P = (F_o^2 + F_c^2)/3$), and all the hydrogen atoms were first found in difference electron density maps, and then placed in the calculated sites and included in the final refinement in the riding model approximation with displacement parameters derived from the parent atoms to which they were bonded. The residual peaks on the final difference Fourier map are 0.573 and $-0.712 \text{ e}/\text{\AA}^3$, respectively.

3 RESULTS AND DISCUSSION

3.1 Crystal structure description

Single-crystal X-ray diffraction analysis reveals that complex **1** crystallizes in monoclinic space, group $C2/c$, and consists of a two-dimensional network. The asymmetric unit contains one Cd(II) atom, one ipm ligand, and one *m*-bdc ligand. In **1**, the Cd(1) atom is six-coordinated with four

carboxylate oxygen atoms from two distinct *m*-bdc ligands, and two nitrogen atoms from one chelating ipm ligand, forming distorted octahedral geometry. For the coordination environment of Cd(1), the Cd(1), O(1), O(2), O(4) and N(2) atoms define the basal plane, and O(3) and N(1) atoms occupy the apical axial positions. The equation of a plane is: $-2.2654(0.0435)x + 14.3131(0.0067)y + 10.0282(0.0107)z = 4.3376(0.0150)$. The deviations of atoms Cd(1), O(2), N(2), O(1), O(2), N(1) and O(3) atoms to the plane are -0.5275 , 0.2042 , 0.5709 , -0.2149 , -0.0327 , 1.5797 and 1.6352 \AA , respectively. The selected bond lengths and bond angles for the title complex are listed in Table 1. The bond distances of Cd(1)–O in **1** are from 2.224(3) to 2.412(3) Å, and the bond distances of Cd(1)–N in **1** fall in the 2.337(4)~2.412(4) Å region, which are similar with the values reported^[15, 16]. The N(O)–Cd–O(N) angles range are from 54.58 to 159.42 °

Table 1. Selected Bond Lengths (Å) and Bond Angles (°) for **1**

Bond	Dist.	Bond	Dist.
Cd(1)–O(1)	2.412(3)	Cd(1)–O(2)	2.358(3)
Cd(1)–O(3) ^A	2.224(3)	Cd(1)–O(4) ^B	2.257(3)
Cd(1)–N(1)	2.337(4)	Cd(1)–N(2)	2.412(4)
Angle	(°)	Angle	(°)
O(2)–Cd(1)–O(1)	54.58(11)	O(3) ^A –Cd(1)–O(2)	116.52(13)
O(4) ^B –Cd(1)–O(2)	85.81(12)	O(3) ^A –Cd(1)–O(1)	85.86(12)
O(4) ^B –Cd(1)–O(1)	137.67(12)	O(3) ^A –Cd(1)–O(4) ^B	101.79(13)
N(1)–Cd(1)–O(2)	83.94(13)	O(3) ^A –Cd(1)–N(1)	159.42(13)
O(3) ^A –Cd(1)–N(2)	92.39(13)	O(4) ^B –Cd(1)–N(1)	80.88(14)
O(4) ^B –Cd(1)–N(2)	121.69(13)	O(2)–Cd(1)–N(2)	136.07(13)
N(1)–Cd(1)–O(1)	106.06(13)	N(2)–Cd(1)–O(1)	99.15(12)
N(1)–Cd(1)–N(2)	69.50(13)		

Symmetry transformations used to generate the equivalent atoms A: $x, -y, z - 1/2$; B: $-x + 1, -y, -z + 1$

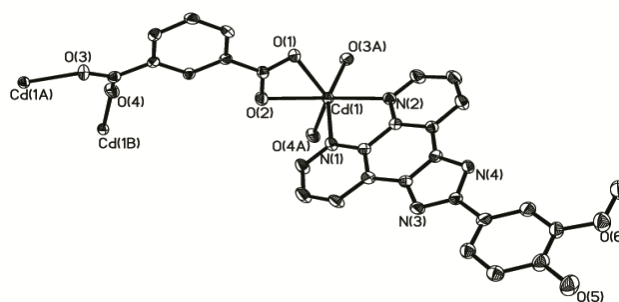


Fig. 1. Molecular structure of complex **1** (Hydrogen atoms were omitted)

As shown in Fig. 2, one *m*-bdc ligand coordinates to three Cd(II) ions through four carboxylic oxygen atoms in two coordination modes: bridging fashion and chelating fashion, which give rise to a 1D double-chain structure. The N-heterocyclic ligands are attached to both sides of this chain

regularly, and the ipm ligands on the same side are parallel nearly.

The hydrogen bond lengths and bond angles for complex **1** are suggested in Table 2. Hydrogen bonding interactions are usually important in the synthesis of supramolecular

architectures. There are two kinds of H-bonding interactions in complex **1**: N–H··O and C–H··O interactions, and the most interesting aspect of the structure concerns the N–H··O hydrogen bonding interactions ($\text{H}(4\text{A})\cdots\text{O}(1) = 2.04 \text{ \AA}$, $\text{N}(4)\cdots\text{O}(1) = 2.867 \text{ \AA}$ and $\text{N}(4)\text{--H}(4\text{A})\cdots\text{O}(4) = 162^\circ$, A: $x, -y, z-1/2$), leading to the 1D chain to a 2D structure (Fig. 3).

Furthermore, there are π – π intersections between the aryl ring of ipm ligands in complex **1** with the distance of $\text{Cg}(1)\cdots\text{Cg}(2)$ ring centroid to be 3.729 \AA ($\text{Cg}(1)$: $\text{C}(1)\text{--}\text{C}(2)\text{--}\text{C}(3)\text{--}\text{C}(4)\text{--}\text{C}(11)\text{--}\text{N}(1)$, $\text{Cg}(2)$: $\text{C}(7)\text{--}\text{C}(8)\text{--}\text{C}(9)\text{--}\text{C}(10)\text{--}\text{C}(12)\text{--}\text{N}(2)$). Clearly, intermolecular π – π stacking and H-bond interactions contribute to the stabilization of the structure of complex **1**.

Table 2. Hydrogen Bond Lengths (Å) and Bond Angles (°) for **1**

D–H··A	D–H	H··A	D··A	D–H··A
N(4)–H(4A)··O(1)	0.86	2.04	2.867(5)	162
O(5)–H(5A)··O(3)	0.82	2.14	2.831(5)	142
C(15)–H(15A)··O(1)	0.93	2.49	3.327(6)	150

Symmetry transformations used to generate the equivalent atoms A: $x, -y, z-1/2$

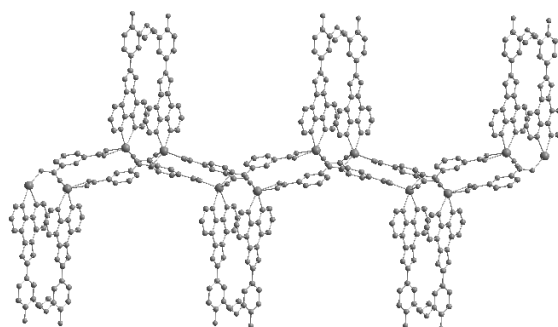


Fig. 2. 1D double-chain structure of complex **1** (Hydrogen atoms were omitted)

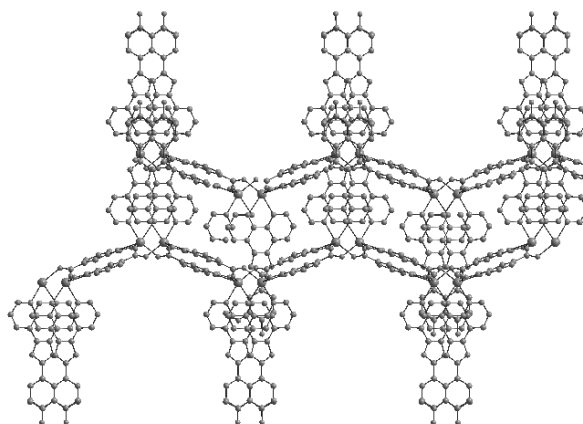


Fig. 3. 2D structure of complex **1** linked by hydrogen bonds

3.2 Thermal analysis

To characterize thermal stability of the title complex, thermal stability property was executed on a NETZSCH STA 449C analyzer. TG curve has been obtained from crystalline samples in the flowing nitrogen atmosphere at a heating rate of $10^\circ\text{C}/\text{min}$. As depicted in Fig. 4, the TG curve of **1** shows that the first weight loss of 25.00% from 269 to 308°C reveals the loss of *m*-bdc molecules (calcd. 25.49%). Upon further heating, a clear weight loss of 60.70% occurs in the temperature range of $308\sim 749^\circ\text{C}$, corresponding to the

release of ipm ligands (calcd. 60.43%).

3.3 XRD spectra

The simulated and experimental power XRD patterns of **1** are shown in Fig. 5. The patterns calculated from the single-crystal X-ray data are in good agreement with the observed ones in almost identical peak position but with different peak intensities, which indicates the phase purity of the products. The differences in intensity may be due to the preferred orientation of the powder samples.

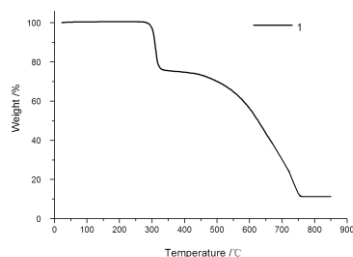


Fig. 4. TG curves of complex **1**

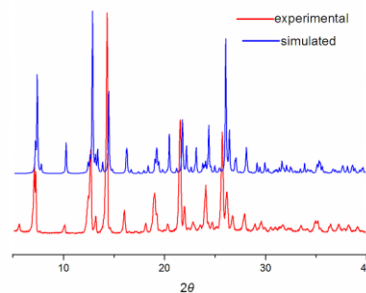


Fig. 5. Experimental and simulated X-ray powder diffraction patterns of complex **1**

3.4 Photoluminescent properties

Metal-organic coordination polymers, especially d^{10} metal centers, such as Ag, Au, Zn and Cd, and conjugated organic linker have been researched because of their fluorescent properties and potential applications of fluorescent-emitting material, chemical sensors and electroluminescent displays. So in this study, we research the luminescence of complex **1** (Fig. 6) in the solid state at room temperature. When excited at 325 nm, complex **1** shows one emission band at 531 nm. To further analyze the nature of these emission bands, the emission properties of ipm were also investigated under the same experimental conditions. The free ligand ipm exhibits one emission band at 495 nm. The results suggest that compared with free ligand, complex **1** is red-shifted by 36 nm

relative to that of ipm. Because the Cd(II) ion with d^{10} configuration is difficult to oxidize or reduce, the emission of these compounds is neither metal-to-ligand charge transfer (MLCT) nor ligand-to-metal charge transfer (LMCT) in nature. The emission of **1** can be mainly ascribed to the intra-ligand $\pi \rightarrow \pi^*$ transition, namely ligand-to-ligand charge transfer (LLCT)^[17-20]. Furthermore, the absolute emission quantum yields determined for complex **1** and ligand ipm are 4.3% and 2.1%, respectively. The results suggested that, compared to the ligand, complex **1** shows higher quantum yield. However, the effect of microenvironment between ligands and complexes on luminous properties needs to be further studied.

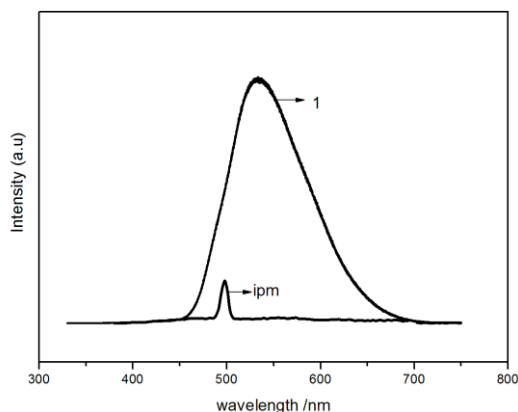


Fig. 6. Luminescent spectrum of ligand ipm and complex **1** in the solid state at room temperature

3.5 Theoretical calculations

The DFT calculations were performed by Gaussian 09 program using the "double- ξ " quality basis set LANL2DZ on Cd atom along with the 6-31g(d, p) basis set on C/H/O/N^[21, 22]. The geometry of complex **1** was fully optimized according to the geometric parameters from X-ray diffraction analysis. The optical and chemical properties are correlated with the detail

of the ground-state electronic structure. The calculated electronic density plots for frontier molecular orbitals were prepared by using the Gauss View 5.0.9 software.

The density diagrams of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are plotted in Fig. 7. It can be seen that HOMO is distributed over the p orbitals of Cd (2.3%) and O atoms

(86.7%). In contrast, LUMO resides mostly on the anti-bonding π^* -orbital of the heterocyclic ligand far more than

98%. Besides, the energy levels of HOMO and LUMO are about -5.15 and -2.03 eV.

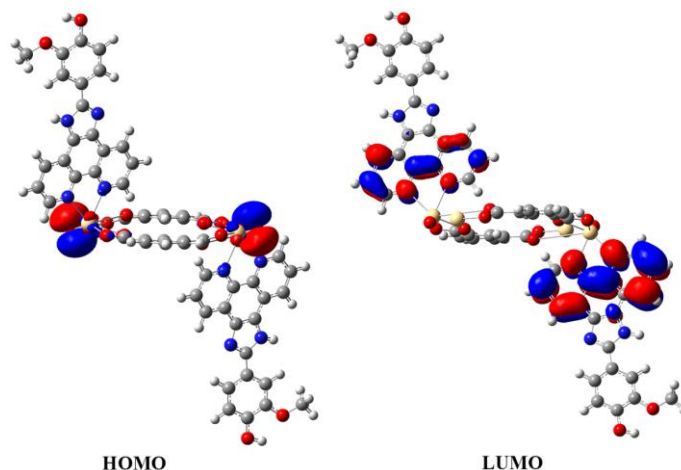


Fig. 7. Molecular orbital diagrams of HOMO and LUMO for complex 1

4 CONCLUSION

In conclusion, a new complex has been synthesized by using plane multifunctional ligands. It is noteworthy that non-covalent interactions (π - π interactions, H-bond and

coordination bonds) can be one of the most powerful forces for directing the supramolecular structures. Complex **1** is very thermal stable and worthy of further study as the candidate of potential photoluminescence material.

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